



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 124 916
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 84200309.7

(51) Int. Cl. 3: C 08 L 71/04
C 09 K 3/28

(22) Date of filing: 05.03.84

(30) Priority: 04.05.83 NL 8301569

(71) Applicant: GENERAL ELECTRIC COMPANY
1 River Road
Schenectady New York 12305(US)

(43) Date of publication of application:
14.11.84 Bulletin 84/46

(72) Inventor: Bussink, Jan
General Electric Plastics B.V. P.O. Box 117
NL-4600 AC Bergen op Zoom(NL)

(84) Designated Contracting States:
BE DE FR GB IT NL SE

(72) Inventor: De Munck, Johannes Wilhelmus J.
General Electric Plastics B.V. P.O. Box 117
NL-4600 AC Bergen op Zoom(NL)

(74) Representative: Grever, Frederik
General Electric Plastics B.V. P.O. Box 117
NL-4600 AC Bergen op Zoom(NL)

(54) Flame retardant polyphenylene ether composition.

(57) The invention relates to a polymer composition based on a polyphenylene ether which is suitable for wire insulation extrusion. The polymer composition comprises a polyphenylene ether, optionally a polystyrene, a hydrogenated block copolymer, an aromatic phosphate compound, a mineral oil and optionally typical additives. The invention also relates to an electrically conductive wire comprising an insulation built up from the above-mentioned polymer composition and provided around the electrically conductive wire by wire insulation extrusion.

EP 0 124 916 A1

Flame retardant polyphenylene ether composition.

The invention relates to a polymer composition having flame-retarding properties, suitable for wire insulation extrusion, based on polyphenylene ether. The invention also relates to an electrically conductive

5 wire having an insulation of synthetic resin which is provided by wire insulation extrusion and is built up from the polymer composition according to the invention.

10 Known polymer compositions for wire insulation extrusion of electrically conductive wires comprise a polymer as a synthetic resin: so far, polyvinyl chloride and polyethylene have been used in particular as a polymer.

15 Special requirements are imposed upon polymer mixtures for wire insulation extrusion: it must be possible to process the mixture by wire insulation extrusion, the mixture must have flame-retarding properties, after the wire insulation extrusion the mixture must have an elongation of more than 100%, the mixture should not be sensitive to strain corrosion and aging and must have a good impact strength. In some 20 applications the requirement is imposed that the polymer mixture may not comprise any halogen atoms.

25 The invention provides a polymer composition based on a polyphenylene ether which satisfies the above-mentioned requirements.

The polymer composition according to the invention is characterized in that it comprises the following constituents: 50-70 parts by weight of polyphenylene ether, 0-20 parts by weight of poly-
5 styrene or a saturated-rubber-modified polystyrene, 25-45 parts by weight of a hydrogenated block copolymer having blocks consisting of homopolymers or copolymers of vinyl aromatic hydrocarbons and having blocks derived from a conjugated diene, 10-20 parts by weight
10 of aromatic phosphate compound, 2-10 parts by weight of mineral oil, 0-10 parts by weight of typical additives.

The polymer compositions according to the invention cannot be formed into an article by injection
15 moulding. When the polymer compositions according to the invention are injection-moulded, delamination occurs. On the other hand, the polymer compositions according to the invention can well be processed by
20 wire insulation extrusion without noticeable delamination occurring.

To be preferred is a polymer composition which comprises 50-65 parts by weight of polyphenylene ether
5-15 parts by weight of homopolystyrene, 30-40 parts by
25 weight of hydrogenated block copolymer, 15-20 parts by weight of aromatic phosphate compound, 4-8 parts by weight of mineral oil and 0-5 parts by weight of the typical additives.

30 Polymer compositions which comprise a polyphenylene ether, polystyrene, or a rubber-modified polystyrene, a hydrogenated block copolymer and an aromatic phosphate compound are known per se. For this purpose, reference may be made to United States Patent
35 Specification 4,143,095 and the German Patent Applica-

tions 24 34 848 and 30 38 551. The polymer compositions described in these patent publications are extruded to pellets and are then formed into an article by injection moulding.

5

These known polymer compositions are not suitable for wire insulation extrusion because in one or more respects they do not satisfy the above-mentioned requirements for materials which are suitable 10 for being provided around an electrical conductor by wire insulation extrusion.

Polymer compositions which comprise a polyphenylene ether, a block copolymer and a mineral 15 oil, are known from the PCT Patent Application WO 81/02020. These known polymer compositions are also extruded to pellets and are formed into articles by means of injection moulding. However, these known 20 polymer compositions are not suitable as a wire insulation for electrical conductors.

Polyphenylene ethers and their preparation are known per se from a large number of patent publications, inter alia from the United States Patent Specifications 3,306,874, 3,306,875, 3,257,357 and 25 3,257,358. The polymer composition according to the invention may comprise one or more of the known polyphenylene ethers, notably also homopolymers and copolymers. The polyphenylene ether in the polymer composition according to the invention preferably 30 comprises units derived from 2,6-dimethyl phenol.

The polymer compositions according to the invention may comprise polystyrenes or a saturated-35 rubbermodified polystyrene. Polystyrene is to be

understood to mean in this Specification homopolymers and copolymers comprising units derived from styrene or substituted styrene compounds, for example alpha-methyl styrene. All the known copolymers of styrene with the exception of the copolymers which comprise unsaturated bonds may be used, for example styrene-acrylonitrile copolymers. Polystyrenes modified with saturated rubbers are known per se. Examples are the polystyrene compounds saturated with EPDM rubber or ethylene-
10 ethylacrylate rubber.

Hydrogenated block copolymers suitable for the polymer compositions according to the invention comprise blocks built up from a vinyl aromatic compound, for example, styrene, and blocks built up from a hydrogenated diene compound, for example butadiene. Suitable are linear block copolymers, radial teleblock copolymers and so-called "tapered" block copolymers, i.e. block copolymers built up from blocks which are bonded together via a "random" copolymer of the vinyl aromatic compound and (hydrogenated) diene compound. Suitable block copolymers are commercially available, for example from Shell under the name of Kraton G.

25 Suitable aromatic phosphate compounds which are present in the polymer compositions according to the invention are described, for example, in United States Patent Specification 4,143,095. Triphenyl phosphate and diphenyl cresyl phosphate may be mentioned in particular.

30 The polymer compositions according to the invention comprise a comparatively large quantity of mineral oil. In combination with the above-mentioned constituents and the above-mentioned relative quan-

tities of the said constituents, a polymer composition is obtained having the properties desired for wire insulation extrusion, due to the presence of the mineral oil. As a mineral oil there may be used aromatic, naphtenic and paraffinic oils or a mixture of one or more of such oils. Paraffinic and/or naphthenic oils are to be preferred.

In addition to the above-mentioned constituents, the polymer compositions according to the invention may also comprise further additives which are typical for compositions comprising polyphenylene ether. Stabilizing additives, for example phosphites, and metal compounds (ZnO, ZnS), dyes and pigments, lubricants may be mentioned in particular.

The invention will now be described in greater detail with reference to the following specific examples:

20 Examples I to XI; comparative examples 1 and 2.

Various polymer compositions were prepared as indicated in Table A hereinafter: the polymer compositions I to XI according to the invention and the polymer compositions 1 and 2 for comparison.

30 The polymer compositions were prepared by dry-mixing the indicated constituents in a mixer until a homogeneous composition was obtained. These homogeneous compositions were then extruded by means of a double blade extruder type Werner-Pfleiderer ZSK 28 having a special kneading and dispersing blade. The blade of the

-6-

extruder was rotated at a speed of 200-400 rpm; the temperature of the extruder was adjusted at 240-320° C; flow rate 5-25 kg per hour. The extrudate was cooled with water and chopped to form a granulate.

5

Test samples were manufactured from the resulting extrudate by injection moulding (T 250-300° C) and a few properties were determined.

10

The various extrudates as mentioned herein-before were provided around an electrically conductive copper wire by means of a wire insulation extrusion device as is generally used to insulate an electrically conductive wire with PVC. The copper wire was preheated 15 at 60-110° C; the extrusion temperature was approximately 250° C. The resulting wire insulation was evaluated for its appearance. The wire insulation was removed from the copper wire and the elongation of the wire insulation was determined (elongation at rupture).

20

All results are recorded in Table B below.

25

From the data of Table B it is apparent that all polymer compositions according to the invention after wire insulation extrusion have a sufficient elongation; the comparative samples have too low an elongation value. It may be seen from a comparison of the results obtained in Examples VIII, IX and X that the use of paraffinic or naphtenic oils is to be preferred instead of aromatic oils. This appears from a more favourable value of the elongation of the insulation. All polymer compositions have good to very good flame retarding properties as appears from the indicated UL (Underwriters Laboratories) 94 and the LOI 30 values.

- 35

TABLE A

TABLE B

Example	1	2	1	II	III	IV	V	VI	VII	VIII	IX	X	XI
Properties of test pieces manufactured by injection moulding													
• Izod impact strength with notch J/m ASTM D 256	61.5	600	595	570	540	550	605	590	610	595	595	615	
• Thermal deformation temperature 1,82 N/mm ² , ASTM D 648 °C	107	126.5	98.5	107.5	87	99.3	82	73.5	80.5	81.5	82	80.5	85
• UL 94 1.6 mm sec.	23-3	17-14	27-15	27-15	41-1	28-13	21-10	13-7	54-7	34-4	36-8	27-4	29-8
• LOI	8	34.5	36	32.8	35	32	33.5	33	34	32	31.5	31	32.8
• Tensile strength at flow DIN 53455 MPa	46.5	45.5	38	41	31	33	34	33	28	32	34	36	33
• Elongation at rupture DIN 53455	8	45	44	68	60	70	76	75	80	106	82	86	70
• Melt viscosity 240° C, 4500 sec ⁻¹ Pa.s	360	500	300	360	240	300	215	170	255	235	240	225	230
Properties insulation after wire insulation extrusion													
• Surface	not smooth	not smooth	good	reasonable	good	not smooth	good	very good	good	good	good	good	good
• Elongation at rupture	8	40	60	100	120	250	120	260	250	350	250	250	300

Claims:

1. A polymer composition having flame-retarding properties, suitable for wire insulation extrusion, based on polyphenylene ether, characterized in that the polymer composition comprises the following constituents: 50-70 parts by weight of polyphenylene ether, 0-20 parts by weight of polystyrene or a saturated-rubber-modified polystyrene, 25-45 parts by weight of a hydrogenated block copolymer having blocks consisting of homopolymers or copolymers of vinyl aromatic hydrocarbons and having blocks derived from a conjugated diene, 10-20 parts by weight of aromatic phosphate compound, 2-10 parts by weight of mineral oil, 0-10 parts by weight of the typical additives.
2. A polymer composition as claimed in Claim 1, characterized in that the composition comprises 50-65 parts by weight of polyphenylene ether, 5-15 parts by weight of homopolystyrene, 30-40 parts by weight of hydrogenated block copolymer, 15-20 parts by weight of aromatic phosphate compound, 4-8 parts by weight of mineral oil and 0-5 parts by weight of the typical additives.
3. An electrically conductive wire comprising an insulation of synthetic resin provided by wire insulation extrusion, characterized in that the insulation of synthetic resin comprising a polymer composition comprising the following constituents: 50-70 parts by weight of polyphenylene ether, 0-20 parts by weight of polystyrene or a saturated-rubber-modified polystyrene, 25-45 parts by weight of a hydrogenated block copolymer having blocks consisting of homopolymers or copolymers of vinyl aromatic hydrocarbons and having blocks derived from a conjugated diene, 10-20 parts by weight of aromatic phosphate compound, 2-10 parts by weight of mineral oil, 0-10 parts by weight of the typical additives.



EUROPEAN SEARCH REPORT

0124916

Application number

EP 84 20 0309

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D, Y	WO-A-8 102 020 (GENERAL ELECTRIC COMPANY) * Claims *	1	C 08 L 71/04 C 09 K 3/28
Y	GB-A-2 060 656 (GENERAL ELECTRIC COMPANY) * Claims * & DE - A - 3 038 551 (Cat. D)	1	
Y	GB-A-2 005 286 (GENERAL ELECTRIC COMPANY) * Claims; page 2, lines 46-50 *	1	
Y	FR-A-2 373 583 (GENERAL ELECTRIC COMPANY) * Claims *	1	
Y	FR-A-2 426 069 (GENERAL ELECTRIC COMPANY) * Claims *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 7) C 08 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 17-07-1984	Examiner MALHERBE Y.J.M.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			